

SCIENCE FOR CERAMIC PRODUCTION

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LITHIUM-BEARING HEAT-RESISTANT CERAMICS (A REVIEW)

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Literature and patent data on the production and use of lithium-bearing heat-resistant ceramics are analyzed; the results of studying the properties of products made of this ceramics are summarized. It is proposed to use the specified ceramics in materials capable of operating under abrupt temperature variations.

The three-component system $\text{Li}_2\text{O} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ is of definite interest for the synthesis of new promising materials with low CLTE values and high resistance to thermal shocks. Materials crystallizing in this system include eucryptite $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, spodumene $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$, and petalite $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{SiO}_2$, which at the temperature of 1200°C have TCLE values of -90×10^{-7} , 9×10^{-7} , and $3 \times 10^{-7} \text{ K}^{-1}$, respectively. Materials synthesized on the basis of the above phases have very high heat resistance [1].

Since ceramic products based on lithium aluminosilicates maintain steady dimensions in a wide temperature interval and withstand sharp temperature changes without being destroyed, they can be used in diverse machinery. Such details are used, for instance, for making frequency-stabilizing elements of klystron generators and hollow resonators of microwave refractometers. The specified materials are also used to make parts for arc chutes, rheostats bodies and other electric equipment, for lining in induction and other types of furnaces, protective cases for thermocouples, and thermostat parts. They are used in applications requiring chemical resistance at high temperatures and products intended for service in nuclear reactors and rocket engines, as well as in making bushings for turbine nozzles and blades.

The use of lithium aluminosilicates in the ceramic industry started in 1930s. It was established that adding 20 – 40% spodumene (here and elsewhere weight content, unless specified otherwise) lowers the refractoriness of material [2]. The introduction of lepidolite and β -spodumene [3] decreases the firing temperature of porcelain by 30 – 40 and 70°C, respectively, due to the formation of low-melting eutectics. An increase in spodumene content is accompanied by increased resistance of porcelain to thermal shocks from 250 to 750°C,

which is due to the increased content of the crystalline phase represented by β -spodumene [4].

The most active research on the application areas of these mineral materials was performed for the purpose of producing heat-resistant materials. The authors of [5] have developed ceramics resistant to thermal shocks produced by hot molding using petalite and kaolin; its TCLE varied within the limits of $(4.0 - 16.0) \times 10^{-7} \text{ K}^{-1}$. To produce ceramics with high resistance to thermal shocks and zero water absorption, petalite combined with spodumene has been used [6]. Materials synthesized only with petalite retain a negative TCLE value up to a temperature of 730°C and the spodumene-based materials – to approximately 400°C. Mixtures prepared using this materials have high thixotropy and are difficult to mold.

Refractory materials have been synthesized on the basis of natural spodumene and, due to their low shrinkage (0.23%), maintain steady sizes [7]. These materials have a low TCLE equal to $(6.7 - 8.9) \times 10^{-7} \text{ K}^{-1}$ in the temperature interval of 20 – 500°C and high heat resistance.

Refractories withstanding 200 cycles of heating to 1300°C with subsequent cooling have been developed with the following composition (%): 50.0 – 80.0 Al_2O_3 , 15.0 – 49.5 SiO_2 , and 0.5 – 6.0 Li_2O [8]. Their synthesis involved alumina-bearing components (bauxite, mullite, refractory clay) and lithium minerals (eucryptite, spodumene, and petalite). The porosity of these refractories is 24.6%, the compressive strength is 141.3 MPa, and the thermal expansion at 650°C is 0.2%.

Furnace saggars have been proposed (patent application Great Britain No. 2372247) containing lithium compounds (oxide or aluminosilicate) in an amount of 2 – 25% (in particular, 10%). They were produced by mixing the refractory component (aluminum oxide), a binder (plastic clay), and

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lithium compounds (spodumene or petalite) with water, subsequent granulation, semidry molding from granules, and firing.

A batch for producing heat-resistant ceramic material called "Stupalite" has been reported to contain lithium aluminosilicates with the $\text{Li}_2\text{O} : \text{Al}_2\text{O}_3 : \text{SiO}_2$ ratio within the limits from 1 : 1 : 3 to 1 : 1 : 8 [9]. The disadvantages of this ceramic is its low electric strength and very narrow (5°C) sintered state interval, which hampers making articles from this mixture.

The authors of [10] have developed a batch for ceramics containing (%): 40 α -spodumene, 23 clay, 22 kaolin, and 15 quartz sand. The disadvantage of this batch is the need to maintain a special cooling regime, as the lithium-containing phase crystallizes in the temperature interval of $1290 - 1270^\circ\text{C}$, which impairs the electric and mechanical parameters of the material and increases its TCLE. These materials have water absorption 0.02%, bending strength 85 MPa, and TCLE equal to $17.0 \times 10^{-7} \text{ K}^{-1}$ in the temperature interval of $20 - 700^\circ\text{C}$.

To make heat-resistant ceramics (Japan patent application No. 3114981) with $\text{TCLE} \pm 20 \times 10^{-7} \text{ K}^{-1}$, a mixture consisting of powders of synthetic β -eucryptite (40–65%), natural clay (15–40%), and natural and (or) synthetic pollucite (10–40%) was moistened with water and mixed. The obtained plastified material was molded according to a required profile, dried, and then sintered.

G. N. Maslennikova and colleagues [11] studying the effect of various spodumene modifications and isothermal exposure on structure and phase formation in lithium-bearing ceramics concluded that it is advisable to use the β -modification of spodumene.

To increase the density of high-strength and highly heat-resistant ceramics, the possibility of modifying the vitreous phase composition by introducing apatite additives containing a set of oxides decreasing viscosity and increasing the reaction capacity of the liquid phase was investigated (USSR Inventor's Certif. No. 899507). As a consequence, a ceramic material was synthesized with the following composition (%): 45–60 β -spodumene, 20–23 clay, 12–18 kaolin, 5–12 quartz sand, and 2–3 apatite. Samples molded from these mixtures were fired at the temperature of 1280°C ; starting with 1000°C firing was performed in a reducing atmosphere. The products had water absorption of 0–0.02%, density $(2.29 - 2.36) \times 10^3 \text{ kg/m}^3$, bending strength 89–96 MPa, and TCLE $(5.1 - 12.6) \times 10^{-7} \text{ K}^{-1}$ in the temperature interval of $20 - 700^\circ\text{C}$.

The results of studying spodumene concentrate [12] for producing insulating materials are published. Spodumene contained in the concentrate remains the main crystalline phase under heat treatment of the mixture. The TCLE of the material is equal to $(1 - 9) \times 10^{-7} \text{ K}^{-1}$ in the interval of $20 - 100^\circ\text{C}$. According to the invention description (USSR Inventor's Certif. No. 977436), the introduction of 5–15% barium carbonate into the spodumene concentrate makes it

possible to raise its static bending strength to 75 MPa. Products made of this material have water absorption 1.5–2.0%, heat resistance 1000°C , and TCLE $(5 - 13) \times 10^{-7} \text{ K}^{-1}$ in the temperature interval of $20 - 500^\circ\text{C}$.

The effect of additives of fritted lithium-bearing glasses on the properties of petalite ceramics has been studied [13]. The material consisting of 90% petalite and 10% glass of the composition (%): 10.7 Li_2O , 8.9 MgO , 8.9 Al_2O_3 , and 71.5 SiO_2 was fired at the temperature of $1250 - 1280^\circ\text{C}$. The material had zero porosity, high resistance to thermal shocks, a low TCLE, and bending strength equal to 90 MPa. Another batch (U.S. patent No. 5962351) consisted of 75–95% minerals and 5–25% lithium aluminosilicate glass powder. The minerals were petalite (40–80%) and clay (10–35%). The obtained glass had the following chemical composition (%): 10–20 Li_2O , 3–15 Al_2O_3 , and 65–85 SiO_2 . The sintered product consisted mainly of β -spodumene and had a TCLE below $10 \times 10^{-7} \text{ K}^{-1}$ in the temperature interval of $0 - 800^\circ\text{C}$.

Another source of lithium oxide that can be used for the synthesis of this class of materials, apart from natural lithium aluminosilicates, is technical lithium carbonate. Researchers at the VNIIEK Institute used chemically pure materials (lithium carbonate, aluminum oxyhydrate, and anhydrous silicic acid) to synthesize materials whose oxide compositions corresponded to eucryptite, spodumene, and petalite [14].

It is established that the synthesis of lithium aluminosilicate from chemically pure materials proceeds in the form of solid-phase reactions; β -eucryptite and β -spodumene are formed under firing to a temperature of $1200 - 1250^\circ\text{C}$ and do not decompose as the temperature is raised up to 1400°C , when melting starts. The formation of petalite proceeds at the temperatures of $1000 - 1200^\circ\text{C}$. An increase in firing temperature leads to the disintegration of petalite, which produces β -eucryptite, β -spodumene, lithium monoaluminate, and high-temperature modifications of quartz (cristobalite and tridimite). The materials have high water absorption (26.6–55.9%) and low strength (14–27 MPa); the TCLE ranges from -32.1×10^{-7} to $10.8 \times 10^{-7} \text{ K}^{-1}$ in the temperature interval of $20 - 700^\circ\text{C}$.

Lithium carbonate, kaolin, and quartz sand were used to synthesize materials [1] corresponding in their oxide ratios to eucryptite (LS-4), petalite (LS-5), and spodumene (LS-9). The studies indicate that synthesis occurs in the solid phase with the formation of β -eucryptite or β -spodumene at lower temperatures ($900 - 1270^\circ\text{C}$) than synthesis in materials based on chemically pure reactants. The structure and phase composition of materials significantly depend on the method of making products. Thus, samples produced of material LS-9 by hot casting, besides β -spodumene, have secondary quartz crystals formed from spodumene, as well as the vitreous phase emerging as a consequence of double firing. The crystalline phase of samples fired at $1200 - 1250^\circ\text{C}$ prepared by extrusion or semidry molding is represented by β -eucryptite, β -spodumene, and a small quantity of secondary quartz.

Materials made of mixture LS-9 withstand over 35 cycles (1000°C – running water) without destruction.

The authors of [15] have developed heat-resistant ceramic materials to produce articles by slip casting into gypsum molds based on the lithium-aluminosilicate system in the crystallization fields of eucryptite, spodumene, and petalite. The considered composition range includes (%): 2.5 – 12.5 Li_2O , 12.5 – 47.5 Al_2O_3 , and 50.0 – 80.0 SiO_2 . The optimum ceramic has water absorption of 14.1%, open porosity 22.0%, and TCLE $0.5 \times 10^{-7} \text{ K}^{-1}$ in the temperature interval of 20 – 400°C.

The crystalline phase in ceramics materials described in [16] is represented by mullite and β -eucryptite in a ratio of 4 : 1, 3 : 2, 2 : 3, and 1 : 4. Mixtures were prepared from Prosyantsovskoe kaolin, lithium carbonate, and technical alumina. The properties of this ceramics determined on extrusion-produced samples are as follows: firing temperature 1350°C, water absorption 0.8%, static bending strength 100 MPa, TCLE $37.0 \times 10^{-7} \text{ K}^{-1}$ in the temperature interval of 20 – 700°C, and heat resistance around 900°C. The samples prepared according to nonplastic technology and fired at 1350°C have water absorption 0.1%, static bending strength 100 MPa, and TCLE of $41.3 \times 10^{-7} \text{ K}^{-1}$ in the temperature interval of 20 – 700°C.

The authors of USSR Inventor's Certif. No. 566802 demonstrated that introducing a $2\text{SrO} \cdot \text{B}_2\text{O}_3$ additive has a favorable effect on heat resistance of lithium ceramics. The investigated material contained (%): 14.5 – 15.1 Li_2CO_3 , 18.9 – 19.6 Al_2O_3 , 61.8 – 64.3 SiO_2 , and 1.0 – 4.8 $2\text{SrO} \cdot \text{B}_2\text{O}_3$. This material was produced from silicon and aluminum oxides and lithium carbonate. The synthesis proceeded in two stages. First Al_2O_3 , SiO_2 , and Li_2CO_3 were mixed by the wet method in a ball mill for 12 – 14 h, then the mixture was dried, granulated, and fired at a temperature of $1300 \pm 20^\circ\text{C}$. The products were molded by hot injection molding, and the final firing was performed at the temperature of $1250 \pm 20^\circ\text{C}$. The bending strength of synthesized materials was 43 – 65 MPa, the TCLE $(2.5 - 3.1) \times 10^{-7} \text{ K}^{-1}$ in the firing temperature of 20 – 200°C.

According to the data in [17], an additive of 3 – 5% apatite makes it possible to lower the firing temperature of lithium-bearing mullite ceramics from 1350°C (water absorption 0.21%) to 1280°C (water absorption 0.37%). In this case, by increasing the degree of milling (from 1.0 to 0.1% residue on No. 0063 sieve) the bending strength of ceramics grows from 75 – 100 to 160 – 165 MPa. The TCLE of the material virtually does not change and is equal to $(30 - 40) \times 10^{-7} \text{ K}^{-1}$ in the temperature interval of 20 – 700°C.

The possibility of using lithium monoaluminate, dialuminate, and silicate as materials for the synthesis of highly heat-resistant lithium-bearing ceramics was investigated in [18]. The advisability of using lithium monoaluminate has been established. The specified mineral combined with quartz sand was used in a two-stage scheme to produce ce-

ramics with a low TCLE ($-47.6 \times 10^{-7} \text{ K}^{-1}$), high heat resistance (950 – 1250°C), and bending strength 20 – 28 MPa. The crystalline phase of these materials is represented by β -eucryptite and β -spodumene. The introduction of BaO and ZnO additives as modifiers decreases the sintering temperature of the materials from 1380 to 1300°C, the TCLE from -47.6×10^{-7} to $-57.5 \times 10^{-7} \text{ K}^{-1}$ in the temperature interval of 20 – 500°C, and water absorption to 3.3%.

There are data on a ceramic material $\text{Li}_{x+1}\text{AlSiO}_{4+x/2}$, where $0 \leq x \leq 0.1$ with a stoichiometric composition (U.S. patent application No. 6066585) based on lithium aluminate, which has negative CLTE values and improved mechanical characteristics.

It is known that β -spodumene is used as an additive modifying the properties of high-temperature ceramics [19]. The introduction of 15% β -spodumene into corundum mixtures leads to the formation of a vitreous phase facilitating liquid-phase sintering. The effect of spodumene additives on heat resistance was studied by estimating it after abrupt chilling of ceramic samples heated to 520°C in water at a temperature of 20°C. A sharp decrease in strength was registered after the thermal shock in monolithic corundum ceramics, whereas the decrease in strength in corundum-spodumene ceramics after the thermal shock was minimal.

The authors of [20] investigated the effect of β -spodumene additives on the technological parameters of raw and presynthesized cordierite batch and the properties of samples obtained. Spodumene was synthesized from lithium carbonate and kaolin; cordierite from talc, kaolin, quartz sand, and alumina. The introduction of 1 – 5% spodumene as a batch additive decreased the TCLE of cordierite ceramics (at a sintering temperature of 1350 – 1400°C in the intervals of 20 – 200°C and 20 – 400°C). At a higher temperature (TCLE measurement interval 20 – 600°C) the effect of introducing spodumene was imperceptible.

Despite substantial achievements in developing theoretical principles for producing lithium-bearing heat-resistant materials and the diversity of its compositions, research in this field is intensely concentrated on searching for new technologies to expand the possibilities of the synthesis of ceramic mixtures. Lately, in the production of high-quality materials, researchers more frequently use sublimated non-aggregated powders with a certain particle shape, as a rule, near-spherical one, and high sintering activity. New methods are used in ceramic technology. For instance, sol-gel technology is extensively used to produce finely dispersed monofractional powders. The advantage of this method is the fact that fragments of future oxide, not only simple but complex oxides as well, are formed already at the gel formation stage, which significantly decreases diffusion obstacles related to solid-phase synthesis and, accordingly, shortens its duration. In this case a homogeneous distribution of components is ensured at the molecular level.

A cost-effective method of sol-gel synthesis has been developed for multicomponent ceramic nanopowders [21]. To

obtain spodumene and mullite powders, metal formates were used with water as a solvent. The averaged particles size of the resulting powders was a few nanometers. At the same time, the powders had a narrow size distribution.

A mixture of SiO_2 and Al_2O_3 sols and a lithium nitrate solution are used in sol-gel synthesis to produce single-phase β -spodumene powders [22]. The initial materials are $\text{Si}(\text{OC}_2\text{H}_5)_4$, $\text{Al}(\text{OC}_4\text{H}_9)_3$, and LiNO_3 . The crystallization temperature of β -spodumene powder gel is around 630°C . Upon heating this gel to $600 - 850^\circ\text{C}$ single-phase crystalline powders of β -spodumene are produced.

A study of sintering ceramics based on β -spodumene powders (LAS) is described in [23], where the powders were preparing according to the sol-gel method using initial materials $\text{Si}(\text{OC}_2\text{H}_5)_4$, $\text{Al}(\text{OC}_4\text{H}_9)_3$, LiNO_3 , and the component facilitating sintering of the material, in this case LiF. The initial LAS powders without LiF had only the crystalline phase β -spodumene. Granules containing less than 4% LiF and sintered at the temperature of 1050°C for 5 h had two crystalline components: β -spodumene and β -eucryptite. After adding 5% LiF the crystalline phases included β -spodumene and triclinic and rhombohedral β -eucryptite. In raising the LiF content from 0.5 to 5.0%, the open porosity decreased from 30.0 to 2.1% and the TCLE from 8.3×10^{-7} to $5.2 \times 10^{-7} \text{ K}^{-1}$.

Contemporary engineering imposes increasingly strict requirements on traditional silicates, which makes it possible to develop materials with a prescribed set of properties. The production of such materials requires the investigation of physicochemical systems, phases formed in them, and their steady combinations. Such research is important not only for understanding and predicting processes occurring in materials, but for solving practical problems related to the selection of compositions and control of the properties of the finished products.

Ceramics resistant to thermal shock can be synthesized on the basis of combinations of crystalline phases of cordierite, mullite, and lithium aluminosilicates (eucryptite, spodumene, and petalite). Ceramic materials whose compositions belong to the system $\text{Li}_2\text{O} - \text{MgO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ not only have high resistance to thermal shocks, but also good mechanical and dielectric properties. According to the data in [24], in the specified system one can synthesize ceramic materials with steadily low TCLE values that have the following composition (%): 1 – 8 Li_2O , 3 – 10 MgO , 42 – 56 Al_2O_3 , and 40 SiO_2 . The main crystalline phases in the materials obtained are cordierite, mullite, and β -eucryptite.

Another study [25] investigates ceramic mixtures based on the four-component system $\text{Li}_2\text{O} - \text{MgO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ in three sections with a constant content of lithium oxide in the amount of 2.5, 5.0, or 7.5%. A rational combination of crystalline phases, in particular spodumene and spinel, is the basis for producing materials with improved thermo-mechanical characteristics. The synthesis of ceramic materi-

als is carried out by sintering samples produced by semidry molding at the temperature of 1200°C . Ceramics of the optimum composition has a TCLE of $10.4 \times 10^{-7} \text{ K}^{-1}$, mechanical strength of 148 MPa, and heat resistance of 126 thermal cycles ($850^\circ\text{C} - \text{running water}$) until losing 20% initial weight.

A ceramic material has been synthesized (USSR Inventor's Certif. No. 288630) with low TCLE values (from -35.0×10^{-7} to $39.9 \times 10^{-7} \text{ K}^{-1}$ in the temperature interval of $20 - 700^\circ\text{C}$) and high static ending strength (55 – 150 MPa). This material contains (%): 1 – 2 Li_2O , 3 – 10 MgO , 42 – 56 Al_2O_3 , and 40 SiO_2 . The initial materials are talc, kaolin, alumina, and lithium carbonate. The mixture is prepared by wet milling in ball mills. The products are produced by molding, hot casting, and extrusion and after drying are fired at a temperature of $1200 - 1300^\circ\text{C}$.

Ceramic materials whose crystalline phase is represented by cordierite and β -eucryptite with a ratio of 4 : 1, 1 : 1, and 1 : 4 have been investigated [26]. They are prepared using talc, lithium carbonate, Prosyantovskoe kaolin, quartz sand, and technical alumina. It has been found that the TCLE increases with decreasing content of eucryptite. The static bending strength of these materials is 20 – 55 MPa.

A heat-resistant ceramic material has been proposed (USSR Inventor's Certif. No. 1310373) that has the following composition (%): 0.91 – 1.21 Li_2O , 14.80 – 15.73 MgO , 3.11 – 4.15 Al_2O_3 , 58.24 – 59.12 SiO_2 , and 20.72 – 22.01 CaO , which is prepared by preliminary synthesis of diopside and spodumene from the batch components. The batch composition for producing diopside is the following (%): 31.87 CaCO_3 , 29.28 MgCO_3 , and 38.85 quartz sand. The batch composition of the mixture for spodumene includes (%): 13.72 Li_2CO_3 , 18.84 alumina, and 67.44 quartz sand. Synthesis is carried out in three stages, milling the resulting products after each stage: the first and the second stage at $1200 - 1250^\circ\text{C}$, the third at $1350 - 1400^\circ\text{C}$ with 1 – 1.5 h exposures at the maximum temperatures. Products are molded from the mixture of synthesized minerals taken in the ratio of 80 – 85% diopside to 15 – 20% spodumene. After molding the products are dried and fired at the temperature of $1200 - 1250^\circ\text{C}$ with 1 – 1.5 h exposure. The properties of the sintered materials are as follows: density $3.86 - 3.89 \text{ g/cm}^3$, porosity 0.16 – 0.19%, acid resistance 98.7 – 99.1%, alkali resistance 96.3 – 96.9%, and heat resistance 59 – 67 thermal cycles ($1000 - 20^\circ\text{C}$) without decreasing mechanical strength.

The possibility of developing heat-resistant composites based on mullite, cordierite, and spodumene has been investigated as well [27]. For the quasibinary sections $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2 - \text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$, $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 - 2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$, and $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 - \text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$ in the system $\text{Li}_2\text{O} - \text{MgO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$, the properties of composites in the eutectic points and near individual components are investigated. It is established that using composites based on mullite combined with cordierite and

spodumene one can obtain materials combining the unique properties of pure materials. Thus, samples containing 60 vol.% cordierite and 40 vol.% mullite at a sintering temperature of 1380°C have a TCLE of $25 \times 10^{-7} \text{ K}^{-1}$ and a Young's modulus of 160 MPa. The properties of samples from compositions based on cordierite and spodumene are no worse than those of ceramics based on pure materials: in the temperature interval of 20–600°C the TCLE of the materials is less than $1.5 \times 10^{-7} \text{ K}^{-1}$, and the samples withstand 100 air–water thermal cycles (800–20°C) without a perceptible decrease in the Young's modulus or formation of visible cracks. The sintering interval has been significantly expanded. The mechanical parameters of samples made of compositions located near the pure materials are also at the level of the mechanical properties of cordierite, spodumene, and mullite.

Ceramics of black color shades have been patented (patent application EPV 1205452) with a TCLE not more than $0.6 \times 10^{-7} \text{ K}^{-1}$ at room temperature, Young's modulus at least 100 GPa, and unit hardness at least 40 MPa · cm³/g. The chemical composition of this ceramic is as follows (%): 0–2.5 Li₂O, 8.0–17.2 MgO, 22.0–38.0 Al₂O₃, 49.5–65.0 SiO₂, and 0.1–2.0 one or more oxides of transition metals. The mass ratio of the ceramic components is: (SiO₂–8Li₂O) : MgO at least 3.0 and (SiO₂–8Li₂O) : Al₂O₃ at least 1.2. The ceramic is obtained by sintering in a nonoxidizing medium (argon, helium, nitrogen, or hydrogen) at a temperature of 1200–1500°C. The initial materials are powders of cordierite, talc, magnesial spinel, magnesium oxide, hydroxide and carbonate, lithium aluminosilicate (petalite, spodumene, eucryptite), lithium hydroxide and carbonate, aluminum oxide, silica, kaolin, and mullite. The ceramics was sintered by hot molding, hot isostatic molding, or under gas pressure.

Japanese patent application No. 3031872 describes ceramic of the composition (%): 0.6–3.5 Li₂O, 2.0–12.0 MgO, 18.0–31.0 Al₂O₃, 55.0–73.0 SiO₂, 0.7–3.0 (K₂O + Na₂O), which is resistant to thermal shocks. To obtain a briquette, a mixture containing (%): 20–60 kaolin, 13–60 lithium silicate, 0–25 feldspar, and 2–12 (converted to oxide) magnesium oxide or another magnesium material was condensed and fired.

Another ceramic material with a low TCLE includes (%): 1.5–6.5 Li₂O, 1.0–10.0 MgO, 14.0–30.5 Al₂O₃, and 58.0–83.0 SiO₂; its main crystalline phase is petalite and (or) spodumene and cordierite (Japanese patent application No. 30331865). To obtain this ceramic material, 30–75% initial lithium silicate was mixed with 20–55% kaolin, 1.5–10.0% magnesial material (for instance, talc) converted to MgO, and 0–15.0 % siliceous material (for instance, quartz) converted to SiO₂, in addition to silica contained in the above-listed initial materials. The mixture was molded and fired at the maximum temperature of 1300°C.

There are data on a material for producing elements for high-precision controlling devices and optical devices and

elements, which need to have high thermal resistance (patent application EPV 1094046). This ceramic has a hexagonal close packing of atoms and consists of crystalline grains that constitute a solid solution of the composition $\text{Mg}_a\text{Li}_b\text{Fe}_c\text{Al}_d\text{Si}_e\text{O}_f$, where $a = 1.8–1.9$; $b = 0.1–0.3$, $c = 0–0.2$, $d = 3.9–4.1$; $e = 6.0–7.0$; and $f = 19–23$. The unit cell parameters of these crystalline grains are: $a = 0.9774–0.9804 \text{ nm}$, $c = 0.9286–0.9330 \text{ nm}$.

The authors of [28] investigate the possibility of creating composite materials based on mullite–cordierite and mullite–spodumene systems. Introducing cordierite and spodumene as lower-melting materials into mullite ceramics makes it possible to lower the sintering temperature of mullite without introducing glass-forming additives. Since cordierite and spodumene have a low TCLE and mullite has high strength, composites based on the specified systems can be used as materials with unique physicochemical properties. The obtained samples have shrinkage of 14.1–19.1%, open porosity 0.11–0.85%, apparent density $(2.27–3.08) \times 10^3 \text{ kg/m}^3$, elasticity modulus 10,611–21,010 GPa, and CLTE $(5.1–44.1) \times 10^{-7} \text{ K}^{-1}$ in the temperature interval of 20–700°C.

Some studies are dedicated to the possibility of increasing chemical and thermal resistance and mechanical characteristics of materials by using modifying additives. A method is known (USSR Inventor's Certif. No. 833847) where CaF₂, ZrO₂, TiO₂, and BaO additives are introduced into mixtures to increase heat resistance and decrease the TCLE. An additive of 0.2–0.6% ZnO (USSR Inventor's Certif. No. 1301819) improves the thermomechanical properties of the emerging vitreous phase. The presence of mineralizing agents P₂O₅ and Fe₂O₃ (USSR Inventor's Certif. No. 409998) and B₂O₃ (Japan patent application No. 3034808) improves the mechanical properties of the materials. Additives used to expand the firing temperature include feldspars, silica, lime, and kaolin (Japanese patent application No. 60-20342).

Using these ceramics materials with unique properties makes it possible to significantly improve the quality of new equipment and machinery.

Thus, the lithium-aluminosilicate system has been used to produce ceramics with a low TCLE ranging from -6×10^{-7} to $9 \times 10^{-7} \text{ K}^{-1}$, which is responsible for their high heat resistance. Porous ceramics withstand temperature differences over 1000°C (for dense ceramic this limit is slightly lower). Such ceramics is produced from natural materials, mainly spodumene. The source of lithium oxide for the synthesis of lithium aluminosilicates is usually Li₂CO₃ and to a lesser extent lithium monoaluminate, dialuminate, and silicate. The use of these compounds makes it possible to expand the list of available materials for lithium-containing ceramics. The temperature of product firing is relatively low and equal to 1200–1250°C, which makes it possible to reduce energy consumption in their production.

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